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CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

INTERNATIONAL APPLICATION NO.  
PCT/EP 98/06394INTERNATIONAL FILING DATE  
8 October 1998PRIORITY DATE CLAIMED  
9 October 1997

TITLE OF INVENTION: COMPOSITE SUITABLE FOR USE IN ELECTROCHEMICAL CELLS

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Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. /X/ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. / / This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. /X/ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. /x / A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. /X/ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a./X/ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b./ / has been transmitted by the International Bureau.
  - c./ / is not required, as the application was filed in the United States Receiving Office (RO/USO).
6. /X/ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. / / Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)).
  - a. / / are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. / / have been transmitted by the International Bureau.
  - c. / / have not been made; however, the time limit for making such amendments has NOT expired.
  - d. / / have not been made and will not be made.
8. / / A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. /X / An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. / / A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern other document(s) or information included:
  11. / / An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
  12. /X / An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
  13. /X / A FIRST preliminary amendment.  
/ / A SECOND or SUBSEQUENT preliminary amendment.
  14. / / A substitute specification.
  15. / / A change of power of attorney and/or address letter.
  16. /x / Other items or information.  
International Search Report  
International Preliminary Examination Report

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PCT/EP 98/06394

ATTORNEY'S DOCKET NO.  
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		CALCULATIONS	PTO USE ONLY
17. /X/ The following fees are submitted			
BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):			
Search Report has been prepared by the EPO or JPO.....	\$840.00	840.00	
International preliminary examination fee paid to USPTO (37 CFR 1.482).....	\$750.00		
No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)).....	\$700.00		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....	\$ 970.00		
International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied pro-visions of PCT Article 35(2)-(4).....	\$96.00		
ENTER APPROPRIATE BASIC FEE AMOUNT =		\$	840.00
Surcharge of \$130.00 for furnishing the oath or declaration later than / 20 / 30 months from the earliest claimed priority date (37 CFR 1.492(e)).			
Claims	Number Filed	Number Extra	Rate
Total Claims	18	-20	X\$18.
Indep. Claims	3	-3	X\$78.
Multiple dependent claim(s) (if applicable)		+270.	
TOTAL OF ABOVE CALCULATION		=	840.00
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).			
SUBTOTAL		=	840.00
Processing fee of \$130. for furnishing the English translation later than / 20 / 30 months from the earliest claimed priority date (37 CFR 1.492(f)). +			
TOTAL NATIONAL FEE		=	840.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) \$40.00 per property =			
TOTAL FEES ENCLOSED		=	\$ 880.00
Amount to be refunded:		\$	
Charged		\$	

- a./X/ A check in the amount of \$ 880. to cover the above fees is enclosed.
- b./ / Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_ to cover the above fees. A duplicate copy of this sheet is enclosed.
- c./X/ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0345. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

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5 We claim:

—13. A composite comprising

- 10 Aa) at least one first layer which comprises a mixture Ia, comprising a mix IIa consisting of
- 15 a) from 1 to 95 % by weight of a solid III, preferably a basic solid III, having a primary particle size of from 5 nm to 20  $\mu$ m and
- b) from 5 to 99 % by weight of a polymeric composition IV obtainable by polymerization of
- 20 b1) from 5 to 100 % by weight, based on the composition IV, of a condensation product V of
- 25  $\alpha$ ) at least one compound VI which is able to condense with a carboxylic acid or a sulfonic acid as defined in  $\beta$  or a derivative or a mixture of two or more thereof, and
- $\beta$ ) at least 1 mol per mol of the compound VI of a carboxylic acid or sulfonic acid VII which contains at least one free-radically polymerizable functional

group, or a derivative thereof or a mixture of two or  
ore thereof,

and

- 5           b2) from 0 to 95 % by weight, based on the composition IV, of  
a further compound VIII having a mean molecular weight  
(number average) of at least 5000 and polyether segments in  
the main chain or a side chain,

10           where the proportion by weight of the mix IIa in the mixture  
Ia is from 1 to 100 % by weight,

and the layer is free of an electron-conducting, electro-  
chemically active compound,

15

and

- B) at least one second layer which comprises a polymeric binder and  
an electron-conducting, electrochemically active compound,

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wherein the first layer or layers and the second layer or layers are joined to  
one another by one of the two methods V1 or V2:

- 25       V1) Lamination of the first layer or layers with the second layer or  
layers under the action of heat or under the action of heat and  
pressure, or

- 30       V2) Corona treatment of the first layer or layers, the second layer or  
layers or the first layer or layers and the second layer or layers and  
subsequent bringing together of the corona-treated first layer or  
layers with the corona-treated second layer or layers.

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## 14. A composite comprising

Ab) at least one first layer which comprises a mixture Ib comprising a mix IIb consisting of

a) from 1 to 95 % by weight of a solid III, preferably a basic solid, having a primary particle size of from 5 nm to 20  $\mu$ m and

b) from 5 to 99 % by weight of a polymer IX obtainable by polymerization of

b1) from 5 to 75 % by weight, based on the polymer IX, of a free-radically polymerizable compound X selected from the group consisting of

olefinic hydrocarbons, (meth)acrylonitrile, halogens containing olefinic compounds, vinyl alcohol, vinyl acetate, N-vinylpyrrolidone, N-vinylimidazole, vinyl formamide, phosphonitrilic chlorides and derivatives thereof which are partly or completely substituted by alkoxy, phenoxy, amino and fluoroalkoxy groups, aromatic olefinic compounds and vinyl ethers, and which is different from the carboxylic acid or the sulfonic acid VII or a derivative thereof, or a mixture of two or more thereof,

and

b2) from 25 to 95 % by weight, based on the polymer IX, of a further compound VIII having a mean molecular weight

(number average) of at least 5000 and polyether segments in the main chain or a side chain,

where the proportion by weight of the mix Ib is from 1 to 100 % by weight

and the layer is free of an electron-conducting, electrochemically active compound,

and

B) at least one second layer which comprises an electron-conducting, electrochemically active compound,

wherein the first layer or layers and the second layer or layers are joined to one another by one of the two methods V1 or V2:

V1) Lamination of the first layer or layers with the second layer or layers under the action of heat or under the action of heat and pressure, or

V2) Corona treatment of the first layer or layers, the second layer or layers or the first layer or layers and the second layer or layers and subsequent bringing together of the corona-treated first layer or layers with the corona-treated or untreated second layer or layers.

15. A composite comprising
- at least one first layer Aa or at least one first layer Ab or at least one first layer Aa and at least one first layer Ab,
- at least one second layer B,
- each as defined in claim 13, and

C) at least one bonding layer.

16. A composite as claimed in claim 15, wherein the bonding layer or layers C  
5 has/have a melting point which is lower than the melting point of the first  
layer or layers or the second layer or layers or the first and second layer or  
layers.
17. A composite as claimed in claim 15, wherein the bonding layer or layers C  
10 is/are a polyethylene oxide, a polyvinyl ether, a polyacrylate, a  
polymethacrylate, polyvinylpyrrolidone, a polyurethane, a wax-like  
(co)polyolefin, a rubber-like material, polyisobutylene or a mixture of two  
or more thereof.
18. A composite as claimed in claim 15, wherein the bonding layer or layers C  
15 comprise(s) a solid III, a plasticizer or a combination of two or more  
thereof.
19. A process for producing a composite as claimed in claim 13, which  
20 comprises joining the first layer or layers and the second layer or layers  
and, if present, the bonding layer or layers to one another by hot  
lamination.
20. A process for producing a composite as claimed in claim 14, which  
25 comprises joining the first layer or layers and the second layer or layers  
and, if present, the bonding layer or layers to one another by hot  
lamination.
21. A process for producing a composite as claimed in claim 13, which  
30 comprises subjecting the first layer or layers or the second layer or layers  
or the first layer or layers and the second layer or layers to a corona

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treatment and subsequently joining the first corona-treated layer or layers to the second corona-treated or untreated layer or layers.

22. A process for producing a composite as claimed in claim 14, which  
5 comprises applying at least one bonding layer to the first layer or layers, the second layer or layers or the first and the second layer or layers and subsequently joining the first layer or layers to the second layer or layers via the bonding layer or layers.
- 10 23. A process for producing a composite as claimed in claim 15, which comprises applying at least one bonding layer to the first layer or layers, the second layer or layers or the first and the second layer or layers and subsequently joining the first layer or layers to the second layer or layers via the bonding layer or layers.
- 15 24. Method of using a composite as claimed in claim 13 electrochemical cell, in a sensor, an electrochromic window, a display, a capacitor or an ion-conducting film.
- 2 25. Method of using a composite as claimed in claim 14 for producing an electrochemical cell, in a sensor, an electrochromic window, a display, a capacitor or an ion-conducting film.
- 25 26. Method of using a composite as claimed in claim 15 for producing an electrochemical cell, in a sensor, an electrochromic window, a display, a capacitor or an ion-conducting film.
- 30 27. An electrochemical cell comprising a composite as claimed in claim 13 or a combination of two or more thereof.

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28. An electrochemical cell comprising a composite as claimed in claim 14 or a combination of two or more thereof.

29. An electrochemical cell comprising a composite as claimed in claim 15 or a  
5 combination of two or more thereof.

30. Method of using the electrochemical cell as claimed in claim 23 as an  
automobile battery, instrument battery, planar battery or polymer battery. --

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10 **Composite suitable for use in electrochemical cells**

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The present invention relates to composites which are suitable for, inter alia, electrochemical cells having electrolytes containing lithium ions; their use in, for example, electrodes; electrodes, sensors, electrochromic windows, 20 displays, capacitors and ion-conducting films comprising such a composite; and also electrochemical cells which comprise such a molding.

Electrochemical, in particular rechargeable, cells are generally known, for example from "Ullmann's Encyclopedia of Industrial Chemistry", 5th Ed., 25 Vol. A3, VCH Verlagsgesellschaft mbH, Weinheim, 1985, pages 343-397.

Among these cells, a special position is occupied by lithium batteries and lithium ion batteries, in particular as secondary cells, owing to their high specific energy storage density.

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As described, for example, in the above citation from "Ullmann", the cathode of such cells comprises lithiated manganese, cobalt, vanadium or nickel mixed oxides which in the stoichiometrically simplest case can be described as  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiCoO}_2$ ,  $\text{LiV}_2\text{O}_5$  or  $\text{LiNiO}_2$ .

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These mixed oxides react reversibly with compounds which can incorporate lithium ions into their lattice, for example graphite, with the lithium ions being removed from the crystal lattice and the metal ions such as manganese, cobalt or nickel ions present in the latter being oxidized. This reaction can be utilized in an electrochemical cell for storing electrical energy by separating the compound which takes up lithium ions, i.e. the anode material, and the lithium-containing mixed oxide, i.e. the cathode material, by means of an electrolyte through which the lithium ions migrate from the mixed oxide into the anode material (charging operation).

The compounds suitable for the reversible storage of lithium ions are usually fixed on collector electrodes by means of a binder.

When the cell is charged, electrons flow through an external voltage source and lithium cations flow through the electrolyte to the anode material. When the cell is used, the lithium cations flow through the electrolyte whereas the electrons flow through a load from the anode material to the cathode material.

To avoid a short circuit within the electrochemical cell, a layer which is electrically insulating but permeable to lithium cations is located between the two electrodes. This layer can be a solid electrolyte or a conventional separator.

In the production of many electrochemical cells, e.g. a lithium ion battery in the form of a round cell, the necessary battery films, i.e. cathode, anode and separator films, are combined using a rolling apparatus to produce a battery roll. In conventional lithium ion batteries, the cathode and anode film(s) are joined to collector electrodes in the form of, for example, an aluminum or copper foil. Such metal foils ensure sufficient mechanical stability.

In contrast, the separator film has to withstand the mechanical stresses on its own, which presents no problem in the case of conventional separator films based on, for example, polyolefins and having the conventional thickness. To further improve the mechanical stability of such conventional separator films, JP 09-134 730 and JP 09-161 815 propose joining these separator films to the anode and/or cathode film by means of a bonding layer.

In contrast to conventional separator films, the mechanical stability of separator films filled with a solid is generally not sufficient to ensure problem-free rolling of the films.

It is an object of the present invention to provide a composite which has at least one layer filled with a solid and is suitable for use in electrochemical cells and is able to withstand the mechanical stresses in the production of, for example, batteries.

We have found that this object is achieved by the composite of the present invention.

This comprises at least one first layer which is filled with a solid, e.g. a separator layer, and at least one second layer which can be a cathode layer or an anode layer. The composite of the present invention thus comprises a separator layer/anode layer combination or separator layer/cathode layer combination or cathode layer/separator layer/anode layer combination; it is of course possible for further layers and/or support materials defined herein to be present.

The present invention accordingly provides, in one embodiment, a composite comprising

Aa) at least one first layer which comprises a mixture Ia, comprising a mix IIa consisting of

a) from 1 to 95% by weight of a solid III, preferably a basic solid III, having a primary particle size of from 5 nm to 20  $\mu$ m and

b) from 5 to 99% by weight of a polymeric composition IV obtainable by polymerization of

b1) from 5 to 100% by weight, based on the composition IV, of a condensation product V of

$\alpha$ ) at least one compound VI which is able to react with a carboxylic acid or a sulfonic acid or a derivative or a mixture of two or more thereof, and

$\beta$ ) at least 1 mol per mol of the compound VI of a carboxylic acid or sulfonic acid VII which contains at least one free-radically polymerizable functional group, or a derivative thereof or a mixture of two or more thereof,

and

b2) from 0 to 95% by weight, based on the composition IV, of a further compound VIII having a mean molecular weight (number average) of at least 5000 and polyether segments in the main chain or a side chain,

where the proportion by weight of the mix IIa in the mixture Ia is from 1 to 100% by weight,

and the layer is free of an electron-conducting,  
electrochemically active compound,

and

B) at least one second layer which comprises an electron-  
conducting, electrochemically active compound,

wherein the first layer or layers and the second layer or layers are  
joined to one another by one of the two methods V1 or V2:

V1) Lamination of the first layer or layers with the second  
layer or layers under the action of heat or pressure or  
under the action of heat and pressure, or

V2) Corona treatment of the first layer or layers, the second  
layer or layers or the first layer or layers and the  
second layer or layers and subsequent bringing together  
of the corona-treated first layer or layers with the  
corona-treated or untreated second layer or layers.

The first layer or layers preferably comprise(s) a mixture Ia comprising a  
mix IIa consisting of

a) from 1 to 95% by weight of a solid III, preferably a basic solid  
III, having a primary particle size of from 5 nm to 20  $\mu$ m and

b) from 5 to 99% by weight of a polymeric composition IV  
obtainable by polymerization of

b1) from 5 to 100% by weight, based on the composition IV, of

a condensation product V of

α) a polyhydric alcohol VI which has carbon and oxygen atoms in the main chain,

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and

β) at least 1 mol per mol of the polyhydric alcohol VI of a  $\alpha,\beta$ -unsaturated carboxylic acid VII,

10

and

b2) from 0 to 95 % by weight, based on the composition IV, of a further compound VIII having a mean molecular weight (number average) of at least 5000 and polyether segments in the main chain or a side chain,

15

where the proportion by weight of the mix IIa in the mixture Ia is from 1 to 100% by weight.

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In a further embodiment, the present invention provides a composite comprising

Ab) at least one first layer which comprises a mixture Ib comprising a mix IIb consisting of

25

a) from 1 to 95% by weight of a solid III, preferably a basic solid, having a primary particle size of from 5 nm to 20  $\mu$ m and

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b) from 5 to 99% by weight of a polymer IX obtainable

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by polymerization of

b1) from 5 to 75% by weight, based on the polymer IX, of  
a free-radically polymerizable compound X which is  
different from the carboxylic acid or the sulfonic acid  
VII or a derivative thereof, or a mixture of two or  
more thereof,

and

b2) from 25 to 95% by weight, based on the polymer IX,  
of a further compound VIII having a mean molecular  
weight (number average) of at least 5000 and polyether  
segments in the main chain or a side chain,

where the proportion by weight of the mix IIb in the mixture  
Ib is from 1 to 100% by weight

and the layer is free of an electron-conducting,  
electrochemically active compound,

and

B) at least one second layer which comprises an electron-  
conducting, electrochemically active compound,

wherein the first layer or layers and the second layer or layers are joined  
to one another by one of the two methods V1 or V2:

V1) Lamination of the first layer or layers with the second  
layer or layers under the action of heat or pressure or

under the action of heat and pressure, or

V2) Corona treatment of the first layer or layers, the second layer or layers or the first layer or layers and the second layer or layers and subsequent bringing together of the corona-treated first layer or layers with the corona-treated second layer or layers.

The present invention further provides a composite comprising

at least one first layer Aa or at least one first layer Ab or at least one first layer Aa and at least one first layer Ab, at least one second layer B, each as defined above, and

C) at least one bonding layer.

The components present in the respective layers of the composite of the present invention are described in more detail below.

first layer A

The solid III used in this layer is, first and foremost, an inorganic solid, preferably an inorganic basic solid, selected from the group consisting of oxides, mixed oxides, silicates, sulfates, carbonates, phosphates, nitrides, amides, imides and carbides of the elements of main groups I, II, III and IV and transition group IV of the Periodic Table; a polymer selected from the group consisting of polyethylene, polypropylene, polystyrene, polytetrafluoroethylene, polyvinylidene fluoride, polyamides, polyimides; a solids dispersion comprising such a polymer; and a mixture of two or more thereof.

Examples which may be mentioned are, in particular: oxides such as

- calcium oxide, silicon dioxide, aluminum oxide, magnesium oxide or titanium dioxide, mixed oxides, for example of the elements silicon, calcium, aluminum, magnesium, titanium; silicates such as ladder, chain, sheet and framework silicates, preferably wollastonite, in particular
- 5 hydrophobicized wollastonite, sulfates such as alkali metal and alkaline earth metal sulfates; carbonates such as alkali metal and alkaline earth metal carbonates, e.g. calcium, magnesium or barium carbonate or lithium, potassium or sodium carbonate; phosphates such as apatites; nitrides; amides; imides; carbides; polymers such as polyethylene, polypropylene, polystyrene,
- 10 polytetrafluoroethylene, polyvinylidene fluoride; polyamides; polyimides; or other thermoplastics, thermosets, microgels, solids dispersions, in particular those comprising the abovementioned polymers, and also mixtures of two or more of the abovementioned solids.
- 15 Furthermore, inorganic solids which conduct Li ions, preferably an inorganic basic solid which conducts Li ions, can be used according to the invention as solid III.

- Examples are: lithium borates such as  $\text{Li}_4\text{B}_6\text{O}_{11} \cdot x\text{H}_2\text{O}$ ,  $\text{Li}_3(\text{BO}_2)_3$ ,
- 20  $\text{Li}_2\text{B}_4\text{O}_7 \cdot x\text{H}_2\text{O}$ ,  $\text{LiBO}_2$ , where x can be from 0 to 20; lithium aluminates such as  $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ,  $\text{Li}_2\text{Al}_2\text{O}_4$ ,  $\text{LiAlO}_2$ ; lithium aluminosilicates such as lithium-containing zeolites, feldspars, feldspar substitutes, phyllosilicates and inosilicates, and, in particular,  $\text{LiAlSi}_2\text{O}_6$  (spodumene),  $\text{LiAlSi}_4\text{O}_{10}$  (petallite),  $\text{LiAlSiO}_4$  (eucryptite), mica such as
- 25  $\text{K}[\text{Li}, \text{Al}]_3[\text{AlSi}]_4\text{O}_{10}(\text{F-OH})_2$ ,  $\text{K}[\text{Li}, \text{Al}, \text{Fe}]_3[\text{AlSi}]_4\text{O}_{10}(\text{F-OH})_2$ ; lithium zeolites, in particular those in fiber, sheet or cube form, in particular those having the formula  $\text{Li}_{2/z}\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$ , where z corresponds to the valence, x is from 1.8 to about 12 and y is from 0 to about 8; lithium carbides such as  $\text{Li}_2\text{C}_2$ ,  $\text{Li}_4\text{C}$ ;  $\text{Li}_3\text{N}$ ; lithium oxides and mixed oxides such
- 30 as  $\text{LiAlO}_2$ ,  $\text{Li}_2\text{MnO}_3$ ,  $\text{Li}_2\text{O}$ ,  $\text{Li}_2\text{O}_2$ ,  $\text{Li}_2\text{MnO}_4$ ,  $\text{Li}_2\text{TiO}_3$ ;  $\text{Li}_2\text{NH}$ ;  $\text{LiNH}_2$ ; lithium phosphates such as  $\text{Li}_3\text{PO}_4$ ,  $\text{LiPO}_3$ ,  $\text{LiAlFPO}_4$ ,  $\text{LiAl}(\text{OH})\text{PO}_4$ ,

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LiFePO<sub>4</sub>, LiMnPO<sub>4</sub>; Li<sub>2</sub>CO<sub>3</sub>; lithium silicates in ladder, chain, sheet and framework form, e.g. Li<sub>2</sub>SiO<sub>3</sub>, Li<sub>2</sub>SiO<sub>4</sub> and Li<sub>6</sub>Si<sub>2</sub>; lithium sulfates such as Li<sub>2</sub>SO<sub>4</sub>, LiHSO<sub>4</sub>, LiKSO<sub>4</sub>; the Li compounds mentioned in the discussion of the cathode layer, with the presence of conductive black being ruled out when they are used as solid III; and also mixtures of two or more of the abovementioned solids which conduct Li ions.

Particularly suitable solids III are basic solids. For the purposes of the present invention, basic solids are those whose mixture with a liquid, water-containing diluent which itself has a pH of at most 7 has a higher pH than this diluent.

The solids are preferably very largely insoluble in the liquid used as electrolyte and electrochemically inert in the battery medium.

Particularly suitable solids are those which have a primary particle size of from 5 nm to 20 μm, preferably from 0.01 to 10 μm and in particular from 0.1 to 5 μm, where the particle sizes specified are determined by electron microscopy. The melting point of the solid is preferably above the operating temperature customary for the electrochemical cell; melting points of above 120°C, in particular above 150°C, have been found to be particularly useful.

In terms of their external shape, the solids can be symmetrical, i.e. have an aspect ratio height: width: length of about 1 and be in the form of spheres, granules, approximately round structures, but also in the form of any polyhedra such as cuboids, tetrahedra, hexahedra, octahedra or bipyramids, or can be distorted or asymmetric, i.e. have an aspect ratio height: width: length different from 1 and be in the form of needles, asymmetric tetrahedra, asymmetric bipyramids, asymmetric hexahedra or octahedra, platelets, disks or as fibers. If the solids are in the form of

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asymmetric particles, the abovementioned upper limit for the primary particle size relates in each case to the smallest axis.

As compound VI which is able to react with a carboxylic acid or a sulfonic acid VII or a derivative or a mixture of two or more thereof, it is possible in principle to use all compounds which fulfill this criterion.

The compound VI is preferably selected from the group consisting of monohydric or polyhydric alcohols having only carbon atoms in the main chain; monohydric or polyhydric alcohols whose main chain comprises at least two carbon atoms plus at least one atom selected from the group consisting of oxygen, phosphorus and nitrogen; silicon-containing compounds; amines having at least one primary amino group; amines having at least one secondary amino group; aminoalcohols; monohydric or polyhydric thiols; compounds containing at least one thiol group and at least one hydroxyl group; and mixtures of two or more thereof.

Among these, preference is in turn given to compounds VI containing two or more functional groups which can react with the carboxylic acid or sulfonic acid.

When compounds VI containing amino groups as functional group are used, preference is given to using those having secondary amino groups so that after condensation/crosslinking there are either absolutely no free NH groups or only small amounts thereof present in the mixture Ia.

Specific examples of preferred compounds are:  
monohydric or polyhydric alcohols which have only carbon atoms in the main chain and have from 1 to 20, preferably from 2 to 20 and in particular from 2 to 10, alcoholic OH groups, in particular dihydric, trihydric and tetrahydric alcohols, preferably having from 2 to 20 carbon

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atoms, e.g. ethylene glycol, 1,2- or 1,3-propanediol, 1,2- or 1,3-butanediol, 1,4-butanediol or 1,4-butyndiol, 1,6-hexanediol, neopentyl glycol, 1,2-dodecanediol, glycerol, trimethylolpropane, pentaerythritol or sugar alcohols, hydroquinone, novolak, bisphenol A; it is also possible, as can be seen from the above definition, to use monohydric alcohols such as methanol, ethanol, propanol, n-, sec- or tert-butyl, etc.; use can also be made of polyhydroxyolefins, preferably those having two terminal hydroxyl groups, e.g.  $\alpha,\omega$ -dihydroxybutadiene;

polyester polyols as are known, for example, from Ullmanns Encyclopädie der technischen Chemie, 4th edition, Volume 19, pp. 62-65 and are obtained, for example, by reaction of dihydric alcohols with polybasic, preferably dibasic, polycarboxylic acids;

monohydric or polyhydric alcohols whose main chain comprises at least two carbon atoms plus at least one oxygen atom, preferably polyether alcohols such as polymerization products of alkylene epoxides, for example isobutylene oxide, propylene oxide, ethylene oxide, 1,2-epoxybutane, 1,2-epoxypentane, 1,2-epoxyhexane, tetrahydrofuran, styrene oxide; use can also be made of polyether alcohols which are modified at the end groups, e.g. polyether alcohols modified by  $\text{NH}_2$  end groups; these alcohols preferably have a molecular weight (number average) of from 100 to 5000, more preferably from 200 to 1000 and in particular from 300 to 800; such compounds are known per se and are commercially available, for example under the trade names Pluriol® or Pluronic® (BASF Aktiengesellschaft);

alcohols as defined above in which some or all carbon atoms are replaced by silicon; compounds of this type which can be used are, in particular, polysiloxanes or alkylene oxide-siloxane copolymers or mixtures of polyether alcohols and polysiloxanes as are described, for example, in EP-B 581 296 and EP-A 525 728; as regards the molecular weight of these alcohols, what has been said above also applies;

alcohols as defined above, in particular polyether alcohols, in which some or all oxygen atoms are replaced by sulfur atoms; with regard to the

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molecular weight of these alcohols, what has been said above likewise applies;

monohydric or polyhydric alcohols whose main chain comprises at least two carbon atoms plus at least one phosphorus atom or at least one nitrogen atom, e.g. diethanolamine and triethanolamine;

lactones which are derived from compounds of the formula  $\text{HO}-(\text{CH}_2)_z-\text{COOH}$ , where  $z$  is from 1 to 20, e.g.  $\epsilon$ -caprolactone,  $\beta$ -propiolactone,  $\gamma$ -butyrolactone or methyl- $\epsilon$ -caprolactone;

silicon-containing compounds such as dichlorosilane or trichlorosilane, phenyltrichlorosilane, diphenyldichlorosilane, dimethylvinylchlorosilane; silanols such as trimethylsilanol;

amines having at least one primary and/or secondary amino group, e.g. butylamine, 2-ethylhexylamine, ethylenediamine, hexamethylenediamine, diethylenetriamine, tetraethylenepentamine, pentaethylenhexamine, aniline, phenylenediamine;

polyetherdiamines such as 4,7-dioxydecane-1,10-diamine, 4,11-dioxytetradecane-1,14-diamine;

monohydric or polyhydric thiols, e.g. aliphatic thiols such as methanethiol, ethanethiol, cyclohexanethiol, dodecanethiol; aromatic thiols such as thiophenol, 4-chlorothiophenol, 2-mercaptoaniline;

compounds containing at least one thiol group and at least one hydroxyl group, e.g. 4-hydroxythiophenol and monothio derivatives of the abovementioned polyhydric alcohols;

amino alcohols such as ethanolamine, N-methylethanolamine, N-ethylethanolamine, N-butylethanolamine, 2-amino-1-propanol, 2-amino-1-phenylethanol, monoamino or polyamino polyols having more than two aliphatically bound hydroxyl groups, e.g. tris(hydroxymethyl)methylamine, glucamine, N,N'-bis(2-hydroxymethyl)ethylenediamine.

It is also possible to use mixtures of two or more of the above-defined compounds VI.

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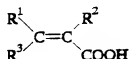
According to the present invention, the abovementioned compounds VI are condensed with a carboxylic acid or sulfonic acid VII which contains at least one free-radically polymerizable functional group or a derivative thereof or a mixture of two or more thereof, in which reaction at least one, preferably all, of the free groups capable of condensation within the compounds VI are condensed with the compound VII.

Carboxylic acids or sulfonic acids VII which can be used for the purposes of the present invention are in principle all carboxylic and sulfonic acids which contain at least one free-radically polymerizable functional group, and also their derivatives. The term "derivatives" used here encompasses both compounds which are derived from a carboxylic or sulfonic acid and in which the acid function is modified, e.g. esters, acid halides or acid anhydrides, and compounds which are derived from a carboxylic or sulfonic acid and in which the carbon skeleton of the carboxylic or sulfonic acid is modified, e.g. halocarboxylic or halosulfonic acids.

Examples of compound VII are, in particular:

$\alpha,\beta$ -unsaturated carboxylic acids or  $\beta,\gamma$ -unsaturated carboxylic acids.

Particularly suitable  $\alpha,\beta$ -unsaturated carboxylic acids are those of the formula



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where  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are hydrogen or  $\text{C}_1$ - $\text{C}_4$ -alkyl radicals; among these, preference is in turn given to acrylic acid and methacrylic acid; other suitable compounds are cinnamic acid, maleic acid, fumaric acid, itaconic acid or p-vinylbenzoic acid, and also derivatives thereof, e.g. anhydrides such as maleic anhydride or itaconic anhydride;

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- halides, in particular chlorides, such as acryloyl or methacryloyl chloride; esters such as (cyclo)alkyl (meth)acrylates having up to 20 carbon atoms in the alkyl radical, e.g. methyl, ethyl, propyl, butyl, hexyl, 2-ethylhexyl, stearyl, lauryl, cyclohexyl, benzyl, trifluoromethyl, hexafluoropropyl or
- 5 tetrafluoropropyl (meth)acrylate, polypropylene glycol mono(meth)acrylates, polyethylene glycol mono(meth)acrylates, poly(meth)acrylates of polyhydric alcohols, e.g. glyceryl di(meth)acrylate, trimethylolpropane di(meth)acrylate, pentaerythritol di- or tri(meth)acrylate, diethylene glycol bis(mono(2-acryloxy-
- 10 ethyl)carbonate), poly(meth)acrylates of alcohols which themselves in turn contain a free-radically polymerizable group, e.g. esters of (meth)acrylic acid and vinyl and/or allyl alcohol;
- vinyl esters of other aliphatic or aromatic carboxylic acids, e.g. vinyl acetate, vinyl propionate, vinyl butyrate, vinyl hexanoate, vinyl octanoate, vinyl decanoate, vinyl stearate, vinyl palmitate, vinyl crotonate, divinyl
- 15 adipate, divinyl sebacate, vinyl 2-ethylhexanoate, vinyl trifluoroacetate; allyl esters of other aliphatic or aromatic carboxylic acids, e.g. allyl acetate, allyl propionate, allyl butyrate, allyl hexanoate, allyl octanoate, allyl decanoate, allyl stearate, allyl palmitate, allyl crotonate, allyl salicylate, allyl lactate, diallyl oxalate, diallyl malonate, allyl- and diallyl succinate, diallyl
- 20 glutarate, diallyl adipate, diallyl pimelate, diallyl cinnamate, diallyl maleate, diallyl phthalate, diallyl isophthalate, triallyl benzene-1,3,5-tricarboxylate, diallyl cinnatricarboxylate, allyl trifluoroacetate, allyl perfluorobutyrate, allyl perfluorooctanoate;
- $\beta$ , $\gamma$ -unsaturated carboxylic acids or their derivatives, e.g. vinylacetic acid,
- 25 2-methylvinylacetic acid, isobutyl 3-butenate, allyl 3-butenate, allyl 2-hydroxy-3-butenate, diketene;
- sulfonic acids such as vinylsulfonic acid, allylsulfonic and methylsulfonic acids, and also their esters and halides, vinyl benzenesulfonate, 4-vinylbenzenesulfonamide.

It is also possible to use mixtures of two or more of the above-described

carboxylic and/or sulfonic acids.

Specific examples of compound X which is capable of free-radical polymerization and can be used for preparing the polymer IX are:

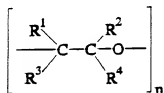
- 5 olefinic hydrocarbons such as ethylene, propylene, butylene, isobutene, hexene or higher homologues and vinylcyclohexane;  
(meth)acrylonitrile;  
halogen-containing olefinic compounds such as vinylidene fluoride, vinylidene chloride, vinyl fluoride, vinyl chloride, hexafluoropropene, trifluoropropene,  
10 1,2-dichloroethylene, 1,2-difluoroethylene and tetrafluoroethylene;  
vinyl alcohol, vinyl acetate, N-vinylpyrrolidone, N-vinylimidazole, vinylformamide;  
phosphonitrilic chlorides such as hexachloro(triphosphazene), and also derivatives thereof which are partially or completely substituted by alkoxy,  
15 phenoxy, amino and fluoroalkoxy groups, i.e. compounds which can be polymerized to form polyphosphazenes;  
aromatic, olefinic compounds such as styrene,  $\alpha$ -methylstyrene;  
vinyl ethers such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, hexyl, octyl, decyl, dodecyl, 2-ethylhexyl, cyclohexyl, benzyl, trifluoromethyl,  
20 hexafluoropropyl and tetrafluoropropyl vinyl ether.

It is, of course, also possible to use mixtures of the above compounds X, resulting in copolymers in which the monomers are, depending on the method of preparation, distributed randomly or arranged in blocks.

Both these compounds X and the condensation products V are polymerized by conventional methods well known to those skilled in the art, preferably polymerized by a free-radical mechanism; as regards the molecular weights obtained, what is said below for the compound VIII applies.

Suitable compounds VIII are, first and foremost, compounds having a mean

molecular weight (number average) of at least 5000, preferably from 5000 to 20,000,000, in particular from 100,000 to 6,000,000, which are able to solvate lithium cations and function as binders. Examples of suitable compounds VIII are polyethers and copolymers which comprise at least 30% by weight of the following structural unit, based on the total weight of the compound VIII:



where R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are aryl groups, alkyl groups, preferably methyl groups, or hydrogen and can be identical or different and contain heteroatoms such as oxygen, nitrogen, sulfur or silicon.

Such compounds are described, for example, in: M.B. Armand et. al., Fast Ion Transport in Solids, Elsevier, New York, 1979, pp. 131-136, or in FR-A 7832976.

The compound VIII can also consist of a mixture of two or more such compounds.

The above-defined polymeric composition IV or the polymer IX can also be in the form of a foam, in which case the solid III is present as a dispersion therein.

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The mixes IIa should, according to the present invention, consist of from 1 to 95% by weight, preferably from 25 to 90% by weight and in particular from 30 to 70% by weight, of a solid III and from 5 to 99% by weight, preferably from 10 to 75% by weight and in particular from 30 to 70% by weight, of a polymeric composition IV, and the compound VIII of the polymeric composition IV should advantageously have a mean molecular weight (number average) of from 5000 to 100,000,000, preferably from 50,000 to 8,000,000. The polymeric composition IV can be obtained by reacting from 5 to 100% by weight, preferably from 30 to 70% by weight, based on the polymeric composition IV, of a compound V with from 0 to 95% by weight, in particular from 30 to 70% by weight, based on the polymeric composition IV, of a compound VIII.

The mixes IIb should, according to the present invention, consist of from 1 to 95% by weight, preferably from 25 to 90% by weight and in particular from 30 to 70% by weight, of a solid III and from 5 to 99% by weight, preferably from 10 to 75% by weight and in particular from 30 to 70% by weight, of a polymer IX, and the compound VIII of the polymer IX should advantageously have a mean molecular weight (number average) of from 5000 to 100,000,000, preferably from 50,000 to 8,000,000. The polymer IX can be obtained by reacting from 5 to 75% by weight, preferably from 30 to 70% by weight, based on the polymer IX, of a compound X with from 25 to 95% by weight, in particular from 30 to 70% by weight, based on the polymer IX, of a compound VIII.

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In the following, the mixtures Ia and Ib used according to the present invention and the mixes IIa and IIb used according to the present invention are discussed together and referred to as "mixture used according to the present invention" and "mix used according to the present invention" respectively.

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To prepare the mixture used according to the present invention which should comprise a mix used according to the present invention in an amount of from 1 to 100% by weight, preferably from 35 to 100% by weight and in particular form 30 to 70% by weight, based on the mixture used according to the present invention, a mixture of a solid III, a condensation product V and, if desired, a compound VIII or a mixture of a solid III, a compound X, a compound VIII and customary additives such as plasticizers, preferably plasticizers comprising polyethylene oxide or polypropylene oxide, can be prepared.

#### second layer B

As polymeric binder used within this second layer B, particular mention may be made of the following polymers:

- 1) Homopolymers, copolymers or block copolymers IVa (polymers IVa) obtainable by polymerization of the above-defined mixtures Ia or Ib.
- 2) Polycarbonates such as polyethylene carbonate, polypropylene carbonate, polybutadiene carbonate, polyvinylidene carbonate.
- 3) Homopolymers, copolymers and block copolymers prepared from
  - a) olefinic hydrocarbons such as ethylene, propylene, butylene, isobutene, propene, hexene or higher homologues, butadiene, cyclopentene, cyclohexene, norbornene, vinylcyclohexane;
  - b) aromatic hydrocarbons such as styrene and methylstyrene;
  - c) esters of acrylic acid or methacrylic acid, e.g. methyl, ethyl, propyl, isopropyl, butyl, isobutyl, hexyl, octyl, decyl, dodecyl, 2-ethylhexyl, cyclohexyl, benzyl, trifluoromethyl, hexafluoropropyl or tetrafluoropropyl acrylate or methacrylate;
  - d) acrylonitrile, methacrylonitrile, N-methylpyrrolidone,

N-vinylimidazole, vinyl acetate;

- e) vinyl ethers such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, hexyl, octyl, decyl, dodecyl, 2-ethylhexyl, cyclohexyl, benzyl, trifluoromethyl, hexafluoropropyl or tetrafluoropropyl vinyl ether;
- f) halogen-containing olefinic compounds such as vinyl chloride, vinyl fluoride, vinylidene fluoride, vinylidene chloride, hexafluoropropene, trifluoropropene, 1,2-dichloroethene, 1,2-difluoroethene, tetrafluoroethene.

4) Polyurethanes, for example obtainable by reacting

- a) organic diisocyanates having from 6 to 30 carbon atoms, for example aliphatic acyclic diisocyanates such as hexamethylene 1,5-diisocyanate and hexamethylene 1,6-diisocyanate, aliphatic cyclic diisocyanates such as cyclohexylene 1,4-diisocyanate, dicyclohexylmethane diisocyanate and isophorone diisocyanate or aromatic diisocyanates such as tolylene 2,4-diisocyanate, tolylene 2,6-diisocyanate, m-tetramethylxylene diisocyanate, p-tetramethylxylene diisocyanate, tetrahydronaphthylene 1,5-diisocyanate and diphenylmethane 4,4'-diisocyanate or mixtures of such compounds,

with

- b) polyhydric alcohols such as polyesterols, polyetherols and diols.

The polyesterols are advantageously predominantly linear polymers having terminal OH groups, preferably those having two or three, in particular two, OH end groups. The acid number of the polyesterols is less than 10 and preferably less than 3. The polyesterols can be prepared in a simple manner by esterification

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of aliphatic or aromatic dicarboxylic acids having from 4 to 15 carbon atoms, preferably from 4 to 6 carbon atoms, with glycols, preferably glycols having from 2 to 25 carbon atoms, or by polymerization of lactones having from 3 to 20 carbon atoms. Examples of dicarboxylic acids which can be used are glutaric acid, pimelic acid, suberic acid, sebacic acid, dodecanoic acid and preferably adipic acid and succinic acid. Suitable aromatic dicarboxylic acids are terephthalic acid, isophthalic acid, phthalic acid or mixtures of these dicarboxylic acids with other dicarboxylic acids, e.g. diphenic acid, sebacic acid, succinic acid and adipic acid. The dicarboxylic acids can be used individually or as mixtures. To prepare the polyesterols, it may be advantageous to use the corresponding acid derivatives such as carboxylic anhydrides or carboxylic chlorides in place of the dicarboxylic acids. Examples of suitable glycols are diethylene glycol, 1,5-pentanediol, 1,10-decanediol and 2,2,4-trimethylpentane-1,5-diol. Preference is given to using 1,2-ethanediol, 1,3-propanediol, 2-methylpropane-1,3-diol, 1,4-butanediol, 1,6-hexanediol, 2,2-dimethylpropane-1,3-diol, 1,4-dimethylcyclohexane, 1,4-diethanolcyclohexane and ethoxylated or propoxylated products of 2,2-bis(4-hydroxyphenyl)propane (bisphenol A). Depending on the desired properties of the polyurethanes, the polyols can be used alone or as a mixture in various mixing ratios. Suitable lactones for preparing the polyesterols are, for example,  $\alpha,\alpha$ -dimethyl- $\beta$ -propiolactone,  $\gamma$ -butyrolactone and preferably  $\epsilon$ -caprolactone.

The polyetherols are essentially linear substances having terminal hydroxyl groups and containing ether bonds. Suitable polyetherols can easily be prepared by polymerization of cyclic ethers such as tetrahydrofuran or by reacting one or more alkylene oxides having

from 2 to 4 carbon atoms in the alkylene radical with an initiator molecule containing two active hydrogen atoms in bound form in the alkylene radical. Examples of suitable alkylene oxides are ethylene oxide, 1,2-propylene oxid, epichlorohydrin, 1,2-butylen oxide and 2,3-butylen oxide. The alkylene oxides can be used individually, alternately in succession or as a mixture. Suitable initiator molecules are, for example, water, glycols such as ethylene glycol, propylene glycol, 1,4-butanediol and 1,6-hexanediol, amines such as ethylenediamine, hexamethylenediamine and 4,4'-diaminodiphenylmethane and aminoalcohols such as ethanolamine. Suitable polyesterols and polyetherols and their preparation are described, for example, in EP-B 416 386; suitable polycarbonatediols, preferably those based on 1,6-hexanediol, and their preparation are described, for example, in US-A 4 131 731.

Use can advantageously be made of up to 30% by weight, based on the total mass of the alcohols, of aliphatic diols having from 2 to 20, preferably from 2 to 10, carbon atoms, e.g. 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,5-pentanediol, 1,10-decanediol, 2-methylpropane-1,3-diol, 2,2-dimethylpropane-1,3-diol, 2-methyl-2-butylpropane-1,3-diol, 2,2-dimethylbutane-1,4-diol, 1,4-dimethylolcyclohexane, neopentyl glycol hydroxypivalate, diethylene glycol, triethylene glycol and methyl-diethanolamine or aromatic-aliphatic or aromatic-cycloaliphatic diols having from 8 to 30 carbon atoms where possible aromatic structures are heterocyclic ring systems or preferably isocyclic ring systems, for example naphthalene or, in particular, benzene derivatives such as bisphenol A, symmetrically diethoxylated bisphenol A, symmetrically dipropoxylated bisphenol A, higher ethoxylated or propoxylated bisphenol A derivatives or bisphenol F derivatives, and also mixtures of such compounds.



Use can advantageously be made of up to 5% by weight, based on the total mass of the alcohols, of aliphatic triols having from 3 to 15, preferably from 3 to 10, carbon atoms, for example trimethylolpropane or glycerol, the reaction product of such compounds with ethylene oxide and/or propylene oxide, and also mixtures of such compounds.

The polyhydric alcohols may bear functional groups, for example neutral groups such as siloxane groups, basic groups such as, in particular, tertiary amino groups or acid groups or their salts or groups which are easily converted into acid groups; these groups are introduced via a polyhydric alcohol. Preference is given to using diol components which bear such groups, e.g. N-methyldiethanolamine, diethyl N,N-bis(hydroxyethyl)aminomethylphosphonate or 3-sulfopropyl N,N-bis(hydroxyethyl)-2-aminoacetate, or dicarboxylic acids which bear such groups and can be used for the preparation of polyesterols, for example 5-sulfoisophthalic acid.

Acid groups are, in particular, the phosphoric acid, phosphonic acid, sulfuric acid, sulfonic acid, carboxyl or ammonium group.

Groups which are easily converted into acid groups are, for example, ester groups or salts, preferably of the alkali metals such as lithium, sodium or potassium.

5) The above-described polyesterols themselves; care should be taken to ensure that molecular weights in the range from 10,000 to 2,000,000, preferably from 50,000 to 1,000,000 are obtained.

6) Polyamines, polysiloxanes and polyphosphazenes, in particular those

which have already been discussed in the description of the polymer IVb.

- 7) Polyetherols as have been described, for example, in the above discussion of the polymer IVa as compound IX or in the discussion of the polyurethanes.

If the layer B is a cathode layer, it comprises an electron-conducting, electrochemically active compound customarily used for cathodes (cathode compound) which is able to release lithium ions on charging, preferably a lithium compound. Particular examples which may be mentioned are:

- $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiNi}_x\text{CO}_y\text{O}_2$ ,  $\text{LiNi}_x\text{CO}_y\text{Al}_z\text{O}_2$ , where  $0 < x, y, z \leq 1$ ,  $\text{Li}_x\text{MnO}_2$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{Mn}_2\text{O}_4$  ( $0 < x \leq 2$ ),  $\text{Li}_x\text{MoO}_2$  ( $0 < x \leq 2$ ),  $\text{Li}_x\text{MnO}_3$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{MnO}_2$  ( $0 < x \leq 2$ ),  $\text{Li}_x\text{Mn}_2\text{O}_4$  ( $0 < x \leq 2$ ),  $\text{Li}_x\text{V}_2\text{O}_4$  ( $0 < x \leq 2.5$ ),  $\text{Li}_x\text{V}_2\text{O}_3$  ( $0 < x \leq 3.5$ ),  $\text{Li}_x\text{VO}_2$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{WO}_2$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{WO}_3$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{TiO}_2$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{Ti}_2\text{O}_4$  ( $0 < x \leq 2$ ),  $\text{Li}_x\text{RuO}_2$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{Fe}_2\text{O}_3$  ( $0 < x \leq 2$ ),  $\text{Li}_x\text{Fe}_3\text{O}_4$  ( $0 < x \leq 2$ ),  $\text{Li}_x\text{Cr}_2\text{O}_3$  ( $0 < x \leq 3$ ),  $\text{Li}_x\text{Cr}_3\text{O}_4$  ( $0 < x \leq 3.8$ ),  $\text{Li}_x\text{V}_3\text{S}_5$  ( $0 < x \leq 1.8$ ),  $\text{Li}_x\text{Ta}_2\text{S}_2$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{FeS}$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{FeS}_2$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{NbS}_2$  ( $0 < x \leq 2.4$ ),  $\text{Li}_x\text{MoS}_2$  ( $0 < x \leq 3$ ),  $\text{Li}_x\text{TiS}_2$  ( $0 < x \leq 2$ ),  $\text{Li}_x\text{ZrS}_2$  ( $0 < x \leq 2$ ),  $\text{Li}_x\text{NbSe}_2$  ( $0 < x \leq 3$ ),  $\text{Li}_x\text{VSe}_2$  ( $0 < x \leq 1$ ),  $\text{Li}_x\text{NiPS}_2$  ( $0 < x \leq 1.5$ ),  $\text{Li}_x\text{FePS}_2$  ( $0 < x \leq 1.5$ ).

If the layer B is an anode layer, it comprises a customary electron-conducting electrochemically active compound known from the prior art (anode compound) which is able to take up lithium ions on charging; particular examples which may be mentioned are:

lithium, lithium-containing metal alloys, micronized carbon black, natural and synthetic graphite, synthetic graphitized carbon powder and carbon fibers, oxides such as titanium oxide, zinc oxide, tin oxide, molybdenum oxide, tungsten oxide, carbonates such as titanium carbonate, molybdenum carbonate and zinc carbonate.

When the layer B is used as anode layer, it further comprises up to 20% by weight, based on the total weight of materials present in it (polymeric binder plus anode compound), of conductive black and, if desired, the abovementioned customary additives. When the layer B is used as cathode or for producing a cathode, it further comprises, based on the total weight of the materials present in it (polymeric binder plus cathode compound), from 0.1 to 20% by weight of conductive black.

### Bonding layer C

As bonding layer C, it is possible in principle to use all materials which are able to join the first layer or layers, as defined above, and the second layer or layers, as defined above, to one another.

The bonding layer is, in particular if the layers in question are joined to one another by hot lamination, generally a material which has a melting point which is lower, preferably from 20 to 50°C lower, than those of the first layer or layers or the second layer or layers or the first layer or layers and the second layer or layers. The melting point of these materials is generally from 25 to 250°C, preferably from 50 to 200°C and in particular from 70 to 180°C.

The bonding layer can also comprise a solid III. The amounts of the solid correspond essentially to the amounts specified for the layers A and B, in each case based on the material forming the bonding layer.

As such materials forming the bonding layer, it is possible to use all materials customarily used as adhesives. Of course, it has to be possible to apply these materials to the layers A and/or B by customary methods of layer formation, for example printing on, casting on, spraying on, extruding, doctor blade coating, etc.

Preference is given to using polymeric compounds as materials forming the bonding layer.

Mention may here be made of:

- 5 melt adhesives such as those based on ethylene-vinyl acetate copolymers which are generally additionally mixed with resins and/or waxes or paraffins so as to vary their melt flow index, those based on low molecular weight (co)polyethylene, atactic (co)polypropylene, ethylene-acrylic ester copolymers and styrene-butadiene and styrene-isoprene block copolymers, polyisobutylene
- 10 and also poly(meth)acrylates and polyesters such as polyethylene terephthalate which can likewise in each case be mixed with plasticizers, in particular those mentioned herein, in order to vary their melt flow index; adhesive plastisols which are essentially mixed from a dispersion of finely divided polyvinyl chloride in plasticizers and low molecular weight materials
- 15 which are reactive under the action of heat and act as bonding agents, e.g. epoxy resin compounds, phenolic resins, etc; heat-sealing adhesives such as those based on copolymers of vinyl chloride or vinylidene chloride, copolymers of vinyl acetate, polymethacrylic esters, polyurethanes and polyesters which can in turn likewise be mixed with other
- 20 polymers or resins; contact adhesives such as those based on natural rubber, synthetic rubber in admixture with resins and solutions of high molecular weight polyurethane elastomers, where the rubber components used are mostly polychloroprene, nitrile or SBR rubbers and the resins used are mainly phenolic resins,
- 25 rosins and also hydrocarbon resins; pressure sensitive adhesives such as those based on synthetic and natural rubbers, poly(meth)acrylic esters, polyvinyl ethers and polyisobutylene, in each case again in combination with modified natural resins, phenol-formaldehyde resins or hydrocarbon resins;
- 30 pressure sensitive dispersion adhesives such as those based on poly(meth)acrylic esters;

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- cold-curing, warm-curing (at from about 80 to about 100°C) and hot-curing (at from about 100 to about 250°C) reaction adhesives such as one-component or two-component polymerization adhesives, where the polymers used for the two-component polymerization adhesives are, in particular,
- 5 synthetic rubbers such as polychloroprene, styrene-butadiene rubber, butyl rubber, polystyrene, polymethacrylates with accelerators such as those based on amines and, for example, benzoyl peroxide as hardener, and examples of one-component polymerization adhesives are those based on cyanoacrylate; epoxy adhesives such as those based on condensation products of
- 10 epichlorohydrin and polyhydric phenols such as bisphenol A; aminoplastics; phenolic resin adhesives; reactive polyurethane adhesives; polymethylol compounds; silicone adhesives; and
- 15 polyimides and polyimidazoles such as polyaminamide and polybenzimidazole.

Specific examples are:

- polyethylene oxide; polyvinyl ethers such as poly(vinyl methyl ether), poly(vinyl ethyl ether), poly(vinyl propyl ether), poly(vinyl butyl ether),
- 20 poly(vinyl isobutyl ether); (co)polyacrylates and (co)polymethacrylates, with preference being given to those having relatively long alkyl chains, e.g. polybutyl (meth)acrylate or polyhexyl (meth)acrylate; polyvinylpyrrolidone; polyurethanes, where the abovementioned polyurethanes can likewise be used; wax-like (co)polyolefins such as polyethylene, polypropylene and polyisoprene
- 25 waxes; rubber-like materials; polyisobutylene; and also mixtures of two or more thereof.

- Further details regarding the materials which can be used according to the present invention in the bonding layer may be found in an article entitled
- 30 "Kleben und Klebstoffe" (Chemie in unserer Zeit, number 4 (1980), and also Ullmann, Encyklopädie der technischen Chemie, 4th edition (1977),

volume 14, pp. 227-268 and also the literature cited therein, whose contents relating to materials having adhesive properties are incorporated by reference into the present application.

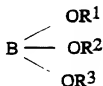
- 5 The layers A and/or B and/or C can further comprise a plasticizer.

Plasticizers which can be used are aprotic solvents, preferably those which solvate Li ions, for example dimethyl carbonate, diethyl carbonate, dipropyl carbonate, diisopropyl carbonate, dibutyl carbonate, ethylene carbonate, 10 propylene carbonate; oligoalkylene oxides such as dibutyl ether, di-tert-butyl ether, dipentyl ether, dihexyl ether, diheptyl ether, dioctyl ether, dinonyl ether, didecyl ether, didodecyl ether, ethylene glycol dimethyl ether, ethylene glycol diethyl ether, 1-tert-butoxy-2-methoxyethane, 1-tert-butoxy-2-ethoxyethane, 1,2-dimethoxypropane, 2-methoxyethyl ether, 2-ethoxyethyl 15 ether, diethylene glycol dibutyl ether, dimethylene glycol tert-butyl methyl ether, triethylene glycol dimethyl ether, tetraethylene glycol dimethyl ether,  $\gamma$ -butyrolactone, dimethylformamide; hydrocarbons of the formula  $C_nH_{2n+2}$  where  $7 < n < 50$ ; organic phosphorus compounds, in particular phosphates and phosphonates such as trimethyl phosphate, triethyl phosphate, 20 tripropyl phosphate, tributyl phosphate, triisobutyl phosphate, tripentyl phosphate, trihexyl phosphate, trioctyl phosphate, tris(2-ethylhexyl) phosphate, tridecyl phosphate, diethyl n-butyl phosphate, tris(butoxyethyl) phosphate, tris(2-methoxyethyl) phosphate, tris(tetrahydrofuryl) phosphate, tris(1H,1H,5H-octafluoropentyl) phosphate, tris(1H,1H-trifluoroethyl) phosphate, tris(2- 25 (diethylamino)ethyl) phosphate, diethyl ethylphosphonate, dipropyl propylphosphonate, dibutyl butylphosphonate, dihexyl hexylphosphonate, dioctyl octylphosphonate, ethyl dimethyl phosphonoacetate, methyl diethyl phosphonoacetate, triethyl phosphonoacetate, dimethyl (2-oxopropyl)phosphonate, diethyl (2-oxopropyl)phosphonate, dipropyl 30 (2-oxopropyl)phosphonate, ethyl diethoxyphosphinylformate, trimethyl phosphonoacetate, triethyl phosphonoacetate, tripropyl phosphonoacetate,

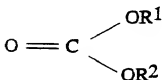
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- tributyl phosphonoacetate; organic sulfur compounds such as sulfates, sulfonates, sulfoxides, sulfones and sulfites, e.g. dimethyl sulfite, diethyl sulfite, glycol sulfite, dimethyl sulfone, diethyl sulfone, diethylpropyl sulfone, dibutyl sulfone, tetramethylene sulfone, methylsulfolane, dimethyl sulfoxide, diethyl sulfoxide, dipropyl sulfoxide, dibutyl sulfoxide, tetramethylene sulfoxide, ethyl methanesulfonate, 1,4-butanediol bis(methanesulfonate), diethyl sulfate, dipropyl sulfate, dibutyl sulfate, dihexyl sulfate, dioctyl sulfate,  $\text{SO}_2\text{CIF}$ ; nitriles such as acrylonitrile;
- dispersants, in particular those having a surfactant structure; and also their mixtures.

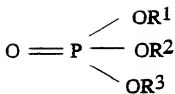
Furthermore, at least one ester of the formulae (E1) to (E5), as shown below, can be used as plasticizer:



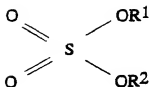
(E1)



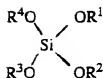
(E2)



(E3)



(E4)



(E5)

where  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$ ,  $\text{R}^4$  are identical or different and are each, independently of one another, a linear or branched  $\text{C}_1$ - $\text{C}_4$ -alkyl group,  $(-\text{CH}_2-\text{CH}_2-\text{O})_n-\text{CH}_3$  where  $n = 1$  to 3, a  $\text{C}_3$ - $\text{C}_6$ -cycloalkyl group, an aromatic hydrocarbon group which may in turn be substituted, with the proviso that at least one of the groups  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  or  $\text{R}^4$  is  $(-\text{CH}_2-\text{CH}_2-\text{O})_n-\text{CH}_3$  where  $n = 1$  to 3.

Among the abovementioned esters of the formulae (E1) to (E5), preference is given to using the phosphoric esters of the formula (E3).

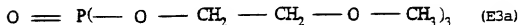
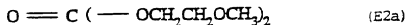
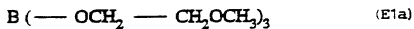
Examples of the groups  $\text{R}^1$ ,  $\text{R}^2$  and, if present,  $\text{R}^3$  and/or  $\text{R}^4$  are the methyl, ethyl, n- and iso-propyl, n- and tert-butyl, cyclopentyl, cyclohexyl and benzyl groups, and also  $(-\text{CH}_2-\text{CH}_2-\text{O})_n-\text{CH}_3$  where  $n = 1$  to 3; however, as already mentioned above, it has to be ensured that at least one of the groups  $\text{R}^1$ ,  $\text{R}^2$ ,  $\text{R}^3$  or  $\text{R}^4$  is  $(-\text{CH}_2-\text{CH}_2-\text{O})_n-\text{CH}_3$  where  $n = 1$  to 3,



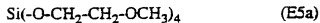
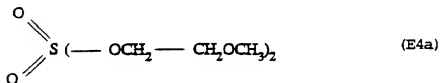
preferably 1 or 2.

Further preference is given to using esters of the formulae (E1) to (E5) in which  $R^1$ ,  $R^2$  and, if present,  $R^3$  and/or  $R^4$  are identical and are  $-\text{CH}_2-\text{CH}_2\text{O}-\text{CH}_3$  or  $(-\text{CH}_2-\text{CH}_2-\text{O})_2-\text{CH}_3$ , with preference again being given to the corresponding phosphoric esters.

Examples of particularly preferred compounds are the compounds of the formulae (E1a) to (E5a):



and



The esters used herein are, in terms of their properties, extraordinarily well suited as plasticizers for the layers in question and generally have a viscosity at room temperature of  $\leq 10\text{mPas}$ , preferably  $\leq 5\text{ mPas}$  and in

particular  $\leq 3$  mPas. They generally have boiling points of about 200°C or above, preferably about 250°C or above and in particular about 300°C or above, in each case measured at atmospheric pressure, and have a sufficiently low vapour pressure of from about  $10^{-5}$  to about  $10^0$  mbar at the temperatures occurring during their use, viz. from about -50°C to about 150°C. As a result of their boiling points, they can be distilled and can thus be produced in high purity. Furthermore, these esters are liquid over a wide temperature range at atmospheric pressure, and are generally still liquid down to a temperature of about -30°C, preferably down to about -40°C. The esters described here can be used as plasticizers and as solvents in electrolyte systems for Li ion accumulators at at least about 80°C, preferably at least about 120°C, more preferably at least about 150°C.

Of course, the esters used according to the invention can also be employed as a mixture with the previously mentioned plasticizers.

Preference is given to combinations which have a sufficiently low viscosity, are able to strongly solvate the ions of the conducting salts, are liquid over a wide temperature range and are sufficiently electrochemically and chemically stable and are also resistant to hydrolysis.

The esters used according to the present invention are prepared by conventional methods, as are described, for example, in K. Mura Kami in Chem. High Polymers (Japan), 7 (1950), pp. 188-193 and in H. Steinberg Organoboron Chemistry, Chapter 5, J. Wiley & Sons, N.Y. 1964. In these preparations, the acids, acid anhydrides or chlorides such as boric acid,  $C(O)Cl_2$ ,  $POCl_3$ ,  $SO_2Cl_2$  and  $SiCl_4$  are used as starting materials and are reacted in a known manner with the appropriate monohydric or polyhydric alcohols or etherols.

The plasticizer content of the respective layer is, based on the mix present

therein or the material making up the layer (polymeric binder plus cathode or anode material), from 0 to 200% by weight, preferably from 0 to 100% by weight and more preferably from 0 to 70% by weight.

- 5 The starting materials used for the respective layers can be dissolved or dispersed in an inorganic or preferably organic liquid diluent, where the resulting solution should have a viscosity of preferably from 100 to 50,000 mPas, and subsequently applied in a known manner, for example by spray coating, casting, dipping, spin coating, roller coating or latterpress, 10 gravure, planographic or screen printing or by extrusion, if desired to a support material, i.e. shaped to form a film-like structure. Further processing can be carried out in a customary way, e.g. by removing the diluent and curing the materials.
- 15 Suitable organic diluents are aliphatic ethers, in particular tetrahydrofuran and dioxane, hydrocarbons, in particular hydrocarbon mixtures such as petroleum spirit, toluene and xylene, aliphatic esters, in particular ethyl acetate and butyl acetate, and ketones, in particular acetone, ethyl methyl ketone and cyclohexanone. It is also possible to use combinations of such 20 diluents.

Suitable support materials are the materials customarily used for electrodes, preferably metals such as aluminum and copper. It is also possible to use coated glass substrates, in particular ITO-coated glass substrates or 25 temporary intermediate supports such as films, in particular polyester films such as polyethylene terephthalate films. Such films can advantageously be provided with a release layer, preferably of polysiloxanes.

Likewise, the production of the individual films which then form the layers 30 within the composite of the present invention can be carried out thermoplastically, for example by injection molding, melt casting, pressing,

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kneading or extrusion, if desired with a subsequent calendaring step.

After film formation, volatile components such as solvents or plasticizers can be removed.

5

If crosslinking of the layers is desired, this can be carried out in a manner known per se, for example by irradiation with ionic or ionizing radiation, an electron beam, preferably at an acceleration voltage of from 20 to 2000 kV and a radiation dose of from 5 to 50 Mrad, UV or visible light, where, in a customary manner, an initiator such as benzil dimethyl ketal or 1,3,5-trimethylbenzoyl-triphenylphosphine oxide can be advantageously added in amounts of, in particular, at most 1% by weight based on the constituents to be crosslinked in the starting materials and the crosslinking can advantageously be carried out over a period of, in general, from 0.5 to 15 minutes, advantageously under inert gas such as nitrogen or argon; by thermal free-radical polymerization, preferably at above 60°C, where an initiator such as azobisisobutyronitrile can advantageously be added in amounts of, in general, at most 5% by weight, preferably from 0.05 to 1% by weight, based on the constituents to be crosslinked in the starting materials; by electrochemically induced polymerization; or by ionic polymerization, for example by acid-catalyzed cationic polymerization, where suitable catalysts are, first and foremost, acids, preferably Lewis acids such as  $\text{BF}_3$  or, in particular,  $\text{LiBF}_4$  or  $\text{LiPF}_6$ . Catalysts containing lithium ions, for example  $\text{LiBF}_4$  or  $\text{LiPF}_6$ , can advantageously remain in the solid electrolyte or separator as conducting salt.

30

The layers described herein can also comprise a dissociable compound containing lithium cations, viz. a conducting salt, and, if desired, further additives such as, in particular, organic solvents, viz. an electrolyte.

Some or all of these materials can be added to the mixture during the

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production of the layer or can be introduced into the layer after production of the latter.

Conducting salts which can be used are the generally known conducting salts which are described, for example, in EP-A 0 096 629. According to the present invention, the conducting salt used is preferably  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiN}(\text{SO}_2\text{C}_n\text{F}_{2n+1})_2$ ,  $\text{LiC}[(\text{C}_n\text{F}_{2n+1})\text{SO}_2]_3$ ,  $\text{Li}(\text{C}_n\text{F}_{2n+1})\text{SO}_3$ , where  $n$  is in each case from 2 to 20,  $\text{LiN}(\text{SO}_2\text{F})_2$ ,  $\text{LiAlCl}_4$ ,  $\text{LiSiF}_6$ ,  $\text{LiSbF}_6$  or a mixture of two or more thereof, with particular preference being given to using  $\text{LiBF}_4$  or  $\text{LiPF}_6$  as conducting salt.

These conducting salts are used in amounts of from 0.1 to 50% by weight, preferably from 0.1 to 20% by weight, in particular from 1 to 10% by weight, in each case based on the material forming the respective layer.

The films/layers forming the composite of the present invention generally have a thickness of from 5 to 500  $\mu\text{m}$ , preferably from 10 to 500  $\mu\text{m}$ , more preferably from 10 to 200  $\mu\text{m}$ . The composite, preferably in the form of a film, generally has a total thickness of from 15 to 1500  $\mu\text{m}$ , in particular a total thickness of from 50 to 500  $\mu\text{m}$ .

Furthermore, the present invention also provides a process for producing a composite, which comprises joining the first layer or layers A and the second layer or layers B and, if present, the bonding layer or layers to one another by lamination under the action of heat or pressure or heat and pressure, preferably by hot lamination. It should be ensured that, depending on the material used for the bonding layer, joining can always be carried out at room temperature or at temperatures up to 50°C or by hot lamination.

In the hot or cold lamination, all customary techniques such as roller melt methods, simple pressing and extrusion lamination can be employed.

In the case of hot lamination, the temperatures used are generally from about 50°C to about 250°C, preferably from about 70°C to about 200°C and more preferably from about 100°C to about 180°C.

A process is also provided for producing a composite, which comprises subjecting the first layer or layers or the second layer or layers or the first layer or layers and the second layer or layers to a corona treatment and subsequently joining the first corona-treated layer or layers to the second corona-treated or untreated layer or layers, preferably by hot lamination.

Corona treatment is a method widely used in surface treatment for roughening/functionalizing surfaces. In this method, the roughening/functionalization is achieved by electrical charging of the surfaces. A generator produces an AC voltage of from about 10 to about 20 KV at a frequency of from about 20 to about 40 KHz and the generator energy is discharged via an electrode system onto the surface of the substrate to be treated, here the layer or layers as defined above, resulting in functionalization/roughening of the treated surface of the layer. According to the present invention, it is preferred for both layers to be corona-treated on the surfaces via which they are to be joined.

Further details regarding the equipment necessary for corona treatment and the procedure for carrying out such treatment may be found in articles in Papier + Kunststoffverarbeitung, number 8 (1980), entitled "Flexible Anpassung der effektiven Kontaktfläche" and Papier + Kunststoffverarbeitung, number 7 (1981), entitled "Oberflächenbehandlungsmethoden zur Haftverbesserung" and the literature cited therein.

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The present invention further provides a process for producing a composite, which comprises applying at least one bonding layer to the first layer or layers, the second layer or layers or the first layer or layers and the second layer or layers and subsequently joining the first layer or layers to the second layer or layers via the bonding layer or layers, preferably by hot lamination.

Furthermore, the present invention provides for the use of a composite, as defined above, for producing an electrochemical cell, in a sensor, an electrochromic window, a display, a capacitor or an ion-conducting film.

It additionally provides an electrochemical cell comprising a composite of the present invention or a combination of two or more thereof.

Suitable organic electrolytes for this purpose are the compounds discussed above under "plasticizers", with preference being given to using the customary organic electrolytes, preferably esters such as ethylene carbonate, propylene carbonate, dimethyl carbonate and diethyl carbonate or mixtures of such compounds.

As can be seen from the above, it is thus readily possible to produce a composite composed of a first electrode layer (e.g. cathode)/if desired, a bonding layer/separator layer/second electrode layer (e.g. anode). Of course, the bonding layer can here also assume the function of a separator, so that the latter can be omitted.

The procedure is, for example, as follows:

An anode material, e.g. graphite, conductive black and PVDF copolymer are first mixed with one another and the resulting mixture is cast onto a Cu foil and subsequently dried (layer 1). Subsequently, a cathode material,

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e.g.  $\text{LiMn}_2\text{O}_4$  or  $\text{LiCoO}_2$ , conductive black and PVDF copolymer are mixed with one another and cast onto an aluminum foil and dried (layer 2). Bringing together the two above-described layers and a separator layer plus, if desired, at least one bonding layer by hot lamination gives a composite which can be used, in combination with any solid and/or liquid electrolyte, as an electrochemical cell.

The filling of such composites with an electrolyte and conducting salt can be carried out either before or preferably after bringing together the layers, if desired after provision of suitable collector electrodes, e.g. a metal foil, and even after introduction of the composite into a battery housing. The particular microporous structure of the layers when using the mixture of the present invention, in particular as a result of the presence of the above-defined solid in the respective layers, makes it possible for the electrolyte and the conducting salt to be taken up and the air in the pores to be displaced. Filling can be carried out at from  $0^\circ\text{C}$  to about  $100^\circ\text{C}$ , depending on the electrolyte used.

The electrochemical cells of the present invention can be used, in particular, as automobile batteries, instrument batteries, planar batteries or polymer batteries.

## EXAMPLES

### 25 Production of an anode foil

400 g of MCMB (Osaka Gas), 35 g of Kynar<sup>®</sup> 2801 (Elf Atochem), 35.6 g of ethylene carbonate and 35.6 g of dimethyl carbonate were added to 460 g of THF. This mixture was milled for a few days and subsequently applied to a copper foil which had previously been painted with an anchor coat. After drying, this foil was used as anode foil for the following



examples.

#### Example 1

- 5 75 g of a wollastonite hydrophobicized with epoxysilane (Tremin<sup>®</sup> 800 EST, from Quarzwerke Frechen) having a particle size of 3  $\mu\text{m}$  was dispersed in 300 g of toluene using a high-speed stirrer. Subsequently, 12.5 g of a polyethylene oxide having a mean molecular weight of  $M_w = 2,000,000$  (Polyol<sup>®</sup>, from Union Carbide), 12.5 g of the methacrylic diester of a  
10 propylene oxide-ethylene oxide block copolymer (Pluriol<sup>®</sup> PE 6000 from BASF AG) and 0.02 g of a UV photoinitiator (Lucirin<sup>®</sup> BDK, from BASF AG) were added to the mixture. The mixture was then applied at 60°C to a silicone-treated polyethylene terephthalate film by means of a doctor blade having a casting slit of 300  $\mu\text{m}$ , the toluene was removed over a period of  
15 5 minutes and peeling off the dried coating gave a film having a thickness of about 30  $\mu\text{m}$  (separator film).

#### Example 2

- 20 The anode foil was powdered with Kynar<sup>®</sup> 2811 (copolymer of vinylidene fluoride and hexafluoropropene, from Elf Atochem) and subsequently, at 160°C, intimately joined to the separator film using a model IL12HR laminator from Ibico.

#### 25 Example 3

- The separator film was powdered on one side with Kynar<sup>®</sup> 2811. The powdered side was laid on the anode foil. The two sheets were subsequently intimately joined to one another at 160°C using the laminator  
30 described in Example 2.

## Example 4

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An aqueous polyethylene dispersion (Polygen® WI1, solids content 35%, from BASF) was applied by means of a doctor blade to an untreated polyethylene terephthalate film. The polyethylene layer applied in this way had a thickness of 2  $\mu\text{m}$ . Subsequently, the dispersion described in Example 1 was cast onto the PET film which had been pretreated in this way. After drying, the separator film formed was detached from the PET film. The polyethylene-coated side of the separator was laid on the anode foil. The two sheets were subsequently intimately joined to one another at 160°C using the laminator.

## Example 5

The procedure of Example 4 was repeated, but 5% of Aerosil® R812 (Degussa), based on the dispersion, were added to the polyethylene dispersion.

## Example 6

The procedure of Example 4 was repeated, but 5% of titanium dioxide T805 (Degussa), based on the dispersion, were added to the polyethylene dispersion.

## Example 7

The procedure of Example 4 was repeated, but 5% of wollastonite Tremin® 939 (Quarzwerke), based on the dispersion, were added to the polyethylene dispersion.

30

## Example 8

A solution of polyethylene oxide in THF was applied by means of a doctor blade to a silicone-treated polyethylene terephthalate film. The polyethylene oxide layer applied in this way had a thickness of 2  $\mu$ m. Subsequently, the dispersion described in Example 1 was cast onto the PET film which had been pretreated in this way. After drying, the separator film was detached from the PET film. The polyethylene oxide-coated side of the separator was laid on the anode foil. The two sheets were subsequently intimately joined to one another at 160°C using the laminator described in Example 2.

10 Example 9

The procedure of Example 8 was repeated, but 5% of Aerosil® R812 (Degussa), based on the solution, were added to the polyethylene oxide solution.

15 Example 10

The procedure of Example 8 was repeated, but 5% of titanium dioxide T805 (Degussa), based on the solution, were added to the polyethylene oxide solution.

Example 11

The procedure of Example 8 was repeated, but 5% of wollastonite Tremin® 939 (Quarzwерke), based on the solution, were added to the polyethylene oxide solution.

Example 12

30 The procedure of Example 8 was repeated, but 3% of propylene carbonate, based on the solution, were added to the polyethylene oxide solution.

### Example 13

The procedure of Example 8 was repeated, but 3% of tris(2-ethylhexyl) phosphate, based on the solution, were added to the polyethylene oxide solution.

### Example 14

The procedure of Example 8 was repeated, but 5% of wollastonite Tremin<sup>®</sup> 939 (Quarzwerke) and 3% of tris(2-ethylhexyl) phosphate, based on the solution, were added to the polyethylene oxide solution.

### Example 15

15 A solution of Acronal<sup>®</sup> 102 (BASF, polybutyl acrylate solution in toluene) was applied by means of a doctor blade to a silicone-treated polyethylene terephthalate film. The polybutyl acrylate layer applied in this way had a thickness of 2  $\mu\text{m}$ .

20 Subsequently, the dispersion described in Example 1 was cast onto the PET film which had been pretreated in this way. After drying, the separator film was detached from the PET film. The polybutyl acrylate-coated side of the separator was laid on the anode foil. The two sheets were subsequently intimately joined to one another at 160°C using the laminator.

### Example 16

30 The procedure of Example 14 was repeated, but 5% of Aerosil<sup>®</sup> R812 (Degussa), based on the solution, were added to the polybutyl acrylate

solution.

#### Example 17

- 5 The procedure of Example 14 was repeated, but 5% of titanium dioxide T805 (Degussa), based on the solution, were added to the polybutyl acrylate solution.

#### Example 18

- 10 The procedure of Example 14 was repeated, but 5% of wollastonite Tremin® 939 (Quarzwirke), based on the solution, were added to the polybutyl acrylate solution.

#### 15 Example 19

- A solution of Oppanol® B200 (BASF, polyisobutylene dissolved in n-hexane) was applied by means of a doctor blade to a silicone-treated polyethylene terephthalate film. The polyisobutylene layer applied in this way had a  
20 thickness of 3  $\mu\text{m}$ . Subsequently, the dispersion described in Example 1 was cast onto the PET film which had been pretreated in this way. After drying, the separator film was detached from the PET film. The polyisobutylene-coated side of the separator was laid on the anode foil. The two sheets were subsequently intimately joined to one another at 160°C  
25 using the laminator.

#### Example 20

- The procedure of Example 18 was repeated, but 5% of Aerosil® R812  
30 (Degussa), based on the solution, were added to the polyisobutylene solution.

Example 21

The procedure of Example 18 was repeated, but 5% of titanium dioxide T805 (Degussa), based on the solution, were added to the polyisobutylene  
5 solution.

Example 22

The procedure of Example 18 was repeated, but 5% of wollastonite Tremin®  
10 939 (Quarzwerke), based on the solution, were added to the polyisobutylene solution.

The qualitative results of testing the composites as described in Examples 1  
to 22 are shown in the following table.

15

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Example	Adhesion	Electrochemical behavior
1	--	+
2	++	++
3	++	+
4	+	+
5	+	+
6	+	+
7	++	+
8	+	++
9	+	++
10	+	++
11	++	++
12	++	++
13	++	++
14	++	+
15	++	+
16	++	+
17	++	++
18	++	+
19	+	+
20	+	++
21	+	++

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Example	Adhesion	Electrochemical behavior
22	++	++

-- unsatisfactory

- acceptable

5 ° satisfactory

+ good

++ excellent

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**Amended set of claims for further prosecution**  
**(clean copy)**

5

We claim:

- 10 1. A composite comprising
- Aa) at least one first layer which comprises a mixture Ia, comprising a  
mix IIa consisting of
- 15 a) from 1 to 95 % by weight of a solid III, preferably a basic  
solid III, having a primary particle size of from 5 nm to 20  
µm and
- b) from 5 to 99 % by weight of a polymeric composition IV  
20 obtainable by polymerization of
- b1) from 5 to 100 % by weight, based on the composition IV, of  
a condensation product V of
- α) at least one compound VI which is able to condense  
25 with a carboxylic acid or a sulfonic acid as defined  
in β or a derivative or a mixture of two or more  
thereof, and
- β) at least 1 mol per mol of the compound VI of a  
30 carboxylic acid or sulfonic acid VII which contains

AMENDED SHEET

at least one free-radically polymerizable functional group, or a derivative thereof or a mixture of two or ore thereof,

and

b2) from 0 to 95 % by weight, based on the composition IV, of a further compound VIII having a mean molecular weight (number average) of at least 5000 and polyether segments in the main chain or a side chain,

where the proportion by weight of the mix IIa in the mixture Ia is from 1 to 100 % by weight,

and the layer is free of an electron-conducting, electrochemically active compound,

and

B) at least one second layer which comprises a polymeric binder and an electron-conducting, electrochemically active compound,

wherein the first layer or layers and the second layer or layers are joined to one another by one of the two methods V1 or V2:

V1) Lamination of the first layer or layers with the second layer or layers under the action of heat or under the action of heat and pressure, or

V2) Corona treatment of the first layer or layers, the second layer or layers or the first layer or layers and the second layer or layers and

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subsequent bringing together of the corona-treated first layer or layers with the corona-treated second layer or layers.

2. A composite comprising

Ab) at least one first layer which comprises a mixture Ib comprising a mix IIb consisting of

a) from 1 to 95 % by weight of a solid III, preferably a basic solid, having a primary particle size of from 5 nm to 20  $\mu$ m and

b) from 5 to 99 % by weight of a polymer IX obtainable by polymerization of

b1) from 5 to 75 % by weight, based on the polymer IX, of a free-radically polymerizable compound X selected from the group consisting of

olefinic hydrocarbons, (meth)acrylonitrile, halogens containing olefinic compounds, vinyl alcohol, vinyl acetate, N-vinylpyrrolidone, N-vinylimidazole, vinyl formamide, phosphonitrilic chlorides and derivatives thereof which are partly or completely substituted by alkoxy, phenoxy, amino and fluoroalkoxy groups, aromatic olefinic compounds and vinyl ethers, and which is different from the carboxylic acid or the sulfonic acid VII or a derivative thereof, or a mixture of two or more thereof,

and

b2) from 25 to 95 % by weight, based on the polymer IX, of a further compound VIII having a mean molecular weight (number average) of at least 5000 and polyether segments in the main chain or a side chain,

where the proportion by weight of the mix Ib is from 1 to 100 % by weight

and the layer is free of an electron-conducting, electrochemically active compound,

and

B) at least one second layer which comprises an electron-conducting, electrochemically active compound,

wherein the first layer or layers and the second layer or layers are joined to one another by one of the two methods V1 or V2:

V1) Lamination of the first layer or layers with the second layer or layers under the action of heat or under the action of heat and pressure, or

V2) Corona treatment of the first layer or layers, the second layer or layers or the first layer or layers and the second layer or layers and subsequent bringing together of the corona-treated first layer or layers with the corona-treated or untreated second layer or layers.

3. A composite comprising

at least one first layer Aa or at least one first layer Ab or at least one first layer Aa and at least one first layer Ab,

at least one second layer B,  
each as defined in claim 1 or 2, and

C) at least one bonding layer.

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4. A composite as claimed in claim 3, wherein the bonding layer or layers C has/have a melting point which is lower than the melting point of the first layer or layers or the second layer or layers or the first and second layer or layers.

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5. A composite as claimed in claim 3 or 4, wherein the bonding layer or layers C is/are a polyethylene oxide, a polyvinyl ether, a polyacrylate, a polymethacrylate, polyvinylpyrrolidone, a polyurethane, a wax-like (co)polyolefin, a rubber-like material, polyisobutylene or a mixture of two or more thereof.

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6. A composite as claimed in any of claims 3 to 5, wherein the bonding layer or layers C comprise(s) a solid III, a plasticizer or a combination of two or more thereof.

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7. A process for producing a composite as claimed in any of claims 1 to 6, which comprises joining the first layer or layers and the second layer or layers and, if present, the bonding layer or layers to one another by hot lamination.

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8. A process for producing a composite as claimed in claim 1 or 2, which comprises subjecting the first layer or layers or the second layer or layers or the first layer or layers and the second layer or layers to a corona treatment and subsequently joining the first corona-treated layer or layers to the second corona-treated or untreated layer or layers.

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9. A process for producing a composite as claimed in any of claims 3 to 6, which comprises applying at least one bonding layer to the first layer or layers, the second layer or layers or the first and the second layer or layers and subsequently joining the first layer or layers to the second layer or layers via the bonding layer or layers.
- 5
10. The use of a composite as claimed in any of claims 1 to 6 for producing an electrochemical cell, in a sensor, an electrochromic window, a display, a capacitor or an ion-conducting film.
- 10
11. An electrochemical cell comprising a composite as claimed in any of claims 1 to 6 or a combination of two or more thereof.
12. The use of the electrochemical cell as claimed in claim 11 as an
- 15 automobile battery, instrument battery, planar battery or polymer battery.

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# Declaration, Power of Attorney

Page 1 of 4

0050/048436

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Composite suitable for use in electrochemical cells

the specification of which

☒ is attached hereto.

☐ was filed on \_\_\_\_\_ as

Application Serial No. \_\_\_\_\_

and amended on \_\_\_\_\_.

☒ was filed as PCT international application

Number PCT/EP98/06394

on 08/10/1998

and was amended under PCT Article 19

on \_\_\_\_\_ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
19744660.4	Germany	09 October 1997	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No

patapct001 - 25

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

\_\_\_\_\_  
(Application Number)

\_\_\_\_\_  
(Filing Date)

\_\_\_\_\_  
(Application Number)

\_\_\_\_\_  
(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.

Filing Date

Status (pending, patented,  
abandoned)

_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

(2)

And we (I) hereby appoint **Messrs. HERBERT B. KEIL**, Registration Number 18,967; and **RUSSELE WEINKAUF**, Registration Number 18,495; the address of both being Messrs. Keil & Weinkauff, 1101 Connecticut Ave., N.W., Washington, D.C. 20036 (telephone 202-659-0100), our attorneys, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to sign the drawings, to receive the patent, and to transact all business in the Patent Office connected therewith.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.



Declaration

Page 3 of 4

0050/048436

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Page 4 of 4

0050/048436

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